Does a Brownian particle equilibrate?

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Abstract. – The conventional equations of Brownian motion can be derived from the first principles to order $\lambda^2 = m/M$, where m and M are the masses of a bath molecule and a Brownian particle respectively. We discuss the extension to order λ^4 using a perturbation analysis of the Kramers-Moyal expansion. For the momentum distribution such method yields an equation whose stationary solution is inconsistent with Boltzmann-Gibbs statistics. This property originates entirely from non-Markovian corrections which are negligible in lowest order but contribute to order λ^4.

Dynamical justification of equilibrium statistical mechanics is a long-standing problem which can be traced to Einstein's criticism of the statistical definition of probability of macrostates [1]. The renewed interest stems primarily from recent development in the theory of nonextensive systems for which the validity of classical Boltzmann-Gibbs (BG) statistics is not obvious. A number of dynamical models generating non-canonical distributions have been suggested lately [2], but for a truly conservative Hamiltonian system deviations from the BG statistics have never been dynamically justified. On the other hand, the BG statistics itself has been recovered directly from dynamics only for a few simplified models. Even for a dilute gas it has been done only in the limit of pair collisions. The *H*-theorem can be readily proved when dynamics is described by the master equation with transition rates obeying the detailed balance condition [3]. The latter can be deduced from reversibility of the microscopic processes involved. However, the master equation is usually a Markovian approximation of an originally non-Markovian exact equation for a targeted variable. The detailed balance arguments do not necessarily apply in this case, as will be discussed at the end of the Letter.

A phenomenon where relaxation to equilibrium may be traced, under reasonable assumptions, from the first principles is Brownian motion of a heavy particle (B particle) of mass M in an infinite bath of light molecules of mass $m \ll M$. Using an appropriate projection operator technique one can get to order $\lambda^2 = m/M$ the Langevin equation (LE) and the corresponding Fokker-Planck equation which describe exponential relaxation of the particle's momentum to the Maxwellian distribution. However, a generalization to higher orders in λ is not trivial and has been studied in detail only for the very special Rayleigh model where the B-particle interacts with ideal gas molecules via the hard-wall potential and the molecules do not interact with each other at all [3, 4].

In this Letter we discuss Brownian motion to order λ^4 in the general case of continuous interaction. The essential difference with the Rayleigh model is that the Langevin equation in general is non-Markovian. However, one may perform systematic expansion around the Markovian limit converting the LE into a local equation with appropriate corrections. To order λ^2 these non-Markovian corrections are negligible, but must be retained to order λ^4. The main result of the Letter is that non-Markovian corrections generate additional terms in the λ^4-order Fokker-Planck equation which make it inconsistent with the BG statistics.

Let us first outline the elements of the dynamical theory of Brownian motion [5, 6]. The basic assumption is that not too far from equilibrium the relation of the particle momentum P and typical momentum of a bath molecule p_m is given by the equipartition theorem, $p_m/P \sim \lambda = \sqrt{m/M}$, and therefore the scaled momentum of the B-particle $p = \lambda P$ is of order λ^0. It is assumed that writing the equation of motion for the scaled momentum p rather than for the true momentum P enables one to extract the overall dependence of the problem on the small parameter λ. Then starting with the exact equation of motion for the B-particle and using an appropriate projection operator and perturbation techniques one can obtain to order λ^2 the non-Markovian LE for the particle's scaled momentum

$$\frac{dp(t)}{dt} = -\lambda^2 \int_0^t d\tau M_0(\tau) p(t - \tau) + \lambda F(t). \tag{1}$$

Here the "random" force $F(t)$ depends on the coordinates and momenta of bath molecules and fluctuates rapidly with mean zero. It is assumed that F may be expanded in powers of λ

$$F(t) = F_0(t) + \lambda F_1(t) + \lambda^2 F_2(t) + \cdots \tag{2}$$

where the first term $F_0(t)$ has a meaning of the force exerted by the bath molecules on the B-particle fixed in space. In other words, $F_0(t)$ is a fluctuating pressure on the infinitely heavy particle. Only this term should be taken into account in the λ^2-order equation, and the fluctuation-dissipation theorem has the form

$$M_0(t) = (\beta/m)\langle F_0(0) F_0(t)\rangle, \tag{3}$$

where β is the inverse temperature of the bath, and the average is taken with respect to canonical distribution of the bath in the field of the B-particle held fixed. Next, noting that $p(t - \tau) = p(t) - \int_{t-\tau}^t dt' \dot{p}(t') = p(t) + O(\lambda)$ one finds that non-Markovian effects are not important at order λ^2, and therefore the LE (1) can be written in the conventional local form

$$\frac{dp(t)}{dt} = -\lambda^2 \gamma_0 \, p(t) + \lambda F_0(t), \tag{4}$$

with $\gamma_0 = \int_0^\infty dt M_0(t)$. Integrating this equation one finds that $\langle p^2(t)\rangle$ relaxes exponentially to the equilibrium value m/β in agreement with BG statistics.

Let us also remind the reader how the Fokker-Planck equation (FPE) for the distribution function $f(p, t)$, corresponding to the LE (4), may be derived. Starting with a generic master equation, which is valid for an arbitrary Markovian process, one can follow the familiar procedure [3] to transform it into the Kramers-Moyal expansion

$$\frac{\partial f(p, t)}{\partial t} = \sum_{n=1} \frac{1}{n!} \left(-\frac{\partial}{\partial p}\right)^n \left\{\alpha_n(p) f(p, t)\right\} \tag{5}$$

where the coefficients are

$$\alpha_n(p) = \lim_{\tau \to 0} \frac{1}{\tau} \langle [p(t + \tau) - p(t)]^n \rangle. \tag{6}$$

These coefficients may be evaluated integrating the LE (4) for small τ,

$$p(t+\tau) - p(t) = -\lambda^2 \gamma_0 \, p(t) \, \tau + \lambda \int_t^{t+\tau} dt' F_0(t'). \tag{7}$$

This formula corresponds to a coarse-grained description with a time resolution much shorter than the relaxation time of the particle's momentum τ_p and much longer than the correlation time for the random force τ_c. One can not require a finer time resolution because the LE itself in the form (4) is valid only on a time scale $t \gg \tau_c$. Two remarks are in order here. First, the route we follow is not a good one when τ_c does not exist, for instance when $C(t) = \langle F_0(0)F_0(t)\rangle \sim t^{-\sigma}$. We ignore the slow hydrodynamic modes of the bath responsible for long-time tails of correlation functions. Second, the coarse-grained description implies that the moments $\langle [p(t+\tau) - p(t)]^n \rangle$ in Eq.(6) must be calculated in the limit $\tau \gg \tau_c$. Only after that must the operation $\lim_{\tau \to 0} \frac{1}{\tau}(\cdots)$ be taken.

In general the "random" force in the LE is neither delta-correlated nor Gaussian, and therefore the Kramers-Moyal expansion is not truncated. However, only the two first terms involve contributions of order λ^2. Then to order λ^2 the expansion turns into the familiar second-order Fokker-Planck equation

$$\frac{\partial f(p,t)}{\partial t} = \lambda^2 D_2 \, f(p,t), \qquad D_2 = a_1 \frac{\partial}{\partial p} p + a_2 \frac{\partial^2}{\partial p^2}. \tag{8}$$

Since the pressure $F_0(t)$ is a stationary process, the coefficients have the form

$$a_1 = \gamma_0 = \frac{\beta}{m} \int_0^\infty dt \, \langle F_0(0)F_0(t)\rangle, \quad a_2 = \frac{1}{2\tau} \int_0^\tau dt_1 \int_0^\tau dt_2 \, \langle F_0(t_1)F_0(t_2)\rangle. \tag{9}$$

Recall that the double integral in the last expression must be taken in the limit $\tau \gg \tau_c$. The subsequent limit $\tau \to 0$ is not necessary because the integral grows linearly with time for $\tau \gg \tau_c$. Indeed, taking into account that $\langle F_0(t_1)F_0(t_2)\rangle = C(|t_1 - t_2|)$ one obtains

$$\int_0^\tau dt_1 \int_0^\tau dt_2 \langle F_0(t_1)F_0(t_2)\rangle = 2 \int_0^\tau dt_1 \int_0^{t_1} dt_2 C(t_1 - t_2) = 2 \int_0^\tau dt_1 (\tau - t_1)C(t_1). \tag{10}$$

For $\tau \gg \tau_c$ this integral equals $2\tau \int_0^\infty dt_1 C(t_1)$. With this result, one finds the relation

$$a_1 = \frac{\beta}{m} a_2. \tag{11}$$

This means that the stationary solution of the equation (8), $f(p) = c \exp\left(-\frac{a_1}{2a_2}p^2\right)$, is Maxwellian.

Our aim is to generalize the above approach to order λ^4. (The λ^3-order damping force vanishes due to symmetry for a homogeneous bath.) The λ^4-order LE has the form

$$\frac{dp(t)}{dt} = -\lambda^2 \int_0^t d\tau \, M_1(\tau)p(t-\tau) - \lambda^4 \int_0^t d\tau \, M_2(\tau)p^3(t-\tau) + \lambda F(t). \tag{12}$$

A microscopic derivation of this equation was recently discussed in detail in [6]. It differs from the λ^2-order LE (1) not only by the presence of the nonlinear damping term involving p^3, but also by additional corrections of order λ^2 to the memory kernel for linear damping

$$M_1(t) = M_0(t) + \lambda^2 \, \delta M(t). \tag{13}$$

Another difference is that the "random" force in Eq. (12) can not be approximated by the pressure term $F_0(t)$, as in the linear LE (4), but must involve the corrections of higher orders F_1 and F_2, see Eq.(2). The correction to the linear damping δM and the nonlinear damping kernel $M_2(t)$ can be expressed in terms of correlation functions involving F_0, F_1 and F_2 [6], but their explicit forms are not important for our purpose here.

Our first step is to find a Markovian approximation for the non-Markovian equation (12) using the same trick as for the linear LE, i.e. writing $\phi(t - \tau) = \phi(t) - \int_{t-\tau}^{t} dt' \dot{\phi}(t')$ for $\phi(t) = p^n(t)$. Since $\frac{d}{dt} p^n(t) \sim \dot{p}(t) = O(\lambda)$ according to (12), the non-Markovian correction for the nonlinear damping is of order λ^5 and should be neglected,

$$-\lambda^4 \int_0^t d\tau \, M_2(\tau) p^3(t - \tau) \to -\lambda^4 p^3(t) \int_0^\infty d\tau \, M_2(\tau) \tag{14}$$

However, for the linear damping term the non-Markovian corrections are of order λ^3 and λ^4 and must be retained. Indeed, let us write the linear damping term as a local expression plus a correction $\Delta(t)$,

$$-\lambda^2 \int_0^t d\tau M_1(\tau) p(t - \tau) = -\lambda^2 p(t) \int_0^t d\tau M_1(\tau) + \Delta(t). \tag{15}$$

The correction

$$\Delta(t) = \lambda^2 \int_0^t d\tau \, M_1(\tau) \int_{t-\tau}^t dt' \, \dot{p}(t') \tag{16}$$

can be evaluated estimating $\dot{p}(t)$ from the LE (12). For $t \gg \tau_c$ one obtains to order λ^4

$$\Delta(t) = \lambda^3 \int_0^t d\tau \, M_0(\tau) \int_{t-\tau}^t dt' F_0(t') - \lambda^4 \, p(t) \int_0^\infty dt \, M_0(t) \int_0^\infty dt \, M_0(t) \, t. \tag{17}$$

We shall write this expression in the form

$$\Delta(t) = \lambda^3 \, F^\star(t) - \lambda^4 \, \gamma^\star \, p(t). \tag{18}$$

Here the first term involves a rapidly changing function

$$F^\star(t) = \frac{\beta}{m} \int_0^t d\tau \, C(\tau) \int_{t-\tau}^t dt' F_0(t') \tag{19}$$

and may be considered as an additional contribution to the random force. Note that $F^\star(t)$ is approximately stationary on the time scale $t \gg \tau_c$. The second term in Eq.(18) with

$$\gamma^\star = \left(\frac{\beta}{m}\right)^2 \int_0^\infty dt \, C(t) \int_0^\infty dt \, C(t) \, t \tag{20}$$

can be interpreted as an additional contribution to the linear damping.

As a result, the LE (12) can be written in local form as follows

$$\frac{dp(t)}{dt} = -\lambda^2 \gamma_1 \, p(t) - \lambda^4 \gamma_2 \, p^3(t) + \lambda \, \xi(t). \tag{21}$$

Here $\xi(t)$ is the "random" force with a λ^2-order non-Markovian correction

$$\xi(t) \;=\; F(t) + \lambda^2 F^\star(t) = F_0(t) + \lambda F_1(t) + \lambda^2 F_2(t) + \lambda^2 F^\star(t). \tag{22}$$

The linear damping coefficient in (21) takes the form

$$\gamma_1 = \gamma_0 + \lambda^2 \, \delta\gamma + \lambda^2 \gamma^\star, \tag{23}$$

with $\delta\gamma = \int_0^\infty dt \, \delta M(t)$, and the nonlinear damping coefficient is $\gamma_2 = \int_0^\infty dt \, M_2(t)$.

Integrating the LE (21) for $\tau_c \ll \tau \ll \tau_p$ one gets

$$p(t+\tau) - p(t) = - \left[\lambda^2 \, \gamma_1 \, p(t) + \lambda^4 \gamma_2 \, p^3(t) \right] \tau + \lambda \int_t^{t+\tau} dt' \xi(t'). \tag{24}$$

Then using Eq.(6) one finds the coefficients α_n in the Kramers-Moyal expansion (5),

$$\alpha_1 = -\lambda^2 \gamma_1 \, p - \lambda^4 \gamma_2 \, p^3 = -\lambda^2 \gamma_0 \, p - \lambda^4 \, \gamma^\star \, p - \lambda^4 \left(\delta\gamma \, p + \gamma_2 \, p^3 \right) \tag{25}$$

and, recalling that $\xi(t)$ is stationary for $t \gg \tau_c$,

$$\alpha_n = \lambda^n \lim_{\tau \to 0} \frac{1}{\tau} \int_0^\tau dt_1 \int_0^\tau dt_2 ... \int_0^\tau dt_n \langle \xi(t_1)\xi(t_2)...\xi(t_n) \rangle \tag{26}$$

for $n = 2, 3, 4$. (The terms with $n > 4$ do not contribute at order λ^4.) In the above expression the integrals must be taken in the limit $\tau \gg \tau_c$.

According to (26), to get α_2 to order λ^4 one needs the correlation $\langle \xi(t_1)\xi(t_2) \rangle$ to order λ^2,

$$\langle \xi(t_1)\xi(t_2) \rangle = \langle F_0(t_1)F_0(t_2) \rangle + \lambda^2 \langle F_0(t_1)F^\star(t_2) \rangle + \lambda^2 \langle F_0(t_2)F^\star(t_1) \rangle$$
$$+ \lambda^2 \langle F_1(t_1)F_1(t_2) \rangle + \lambda^2 \langle F_0(t_1)F_2(t_2) \rangle + \lambda^2 \langle F_0(t_2)F_2(t_1) \rangle.$$

Similarly, α_3 and α_4 require the correlations to order λ^1 and λ^0, respectively:

$$\langle \xi(t_1)\xi(t_2)\xi(t_3) \rangle = \lambda \langle F_0(t_1)F_0(t_2)F_1(t_3) \rangle + \lambda \langle F_0(t_1)F_1(t_2)F_0(t_3) \rangle + \lambda \langle F_1(t_1)F_0(t_2)F_0(t_3) \rangle,$$
$$\langle \xi(t_1)\xi(t_2)\xi(t_3)\xi(t_4) \rangle = \langle F_0(t_1)F_0(t_2)F_0(t_3)F_0(t_4) \rangle.$$

Using these formulas and collecting the terms of the same order, one obtains the λ^4-order FPE in the form

$$\frac{\partial f(p,t)}{\partial t} = \left\{ \lambda^2 D_2 + \lambda^4 D_2^\star + \lambda^4 D_4 \right\} f(p,t). \tag{27}$$

Here the differential operator D_2 is the same as in the λ^2-order FPE (8). The operator $D_2^\star$ originates from non-Markovian corrections and has the same structure as D_2,

$$D_2^\star = b_1 \frac{\partial}{\partial p} p + b_2 \frac{\partial^2}{\partial p^2} \tag{28}$$

with $b_1 = \gamma^\star$ given by Eq.(20) and

$$b_2 = \frac{1}{2\tau} \int_0^\tau \int_0^\tau dt_1 dt_2 \left\{ \langle F^\star(t_1)F_0(t_2) \rangle + \langle F^\star(t_2)F_0(t_1) \rangle \right\} = \frac{1}{\tau} \int_0^\tau \int_0^\tau dt_1 \, dt_2 \langle F^\star(t_2)F_0(t_1) \rangle. \tag{29}$$

The operator D_4 in Eq.(27) is a differential operator of order four. It absorbs the terms of order λ^4 which are expressed in terms of time correlations $\langle F_0 F_2 \rangle$, $\langle F_1 F_1 \rangle$, $\langle F_0 F_0 F_1 \rangle$, and $\langle F_0 F_0 F_0 F_0 \rangle$. Since $\langle F_i(t) \rangle = 0$, the first three of these correlations are actually cumulants, which we denote by $\langle\!\langle \cdots \rangle\!\rangle$,

$$\langle F_i F_j \rangle \equiv \langle F_i \rangle \langle F_j \rangle + \langle\!\langle F_i F_j \rangle\!\rangle = \langle\!\langle F_i F_j \rangle\!\rangle,$$
$$\langle F_i F_j F_k \rangle \equiv \langle F_i \rangle \langle F_j \rangle \langle F_k \rangle + \langle F_i \rangle \langle\!\langle F_j F_k \rangle\!\rangle + \langle F_j \rangle \langle\!\langle F_i F_k \rangle\!\rangle + \langle F_k \rangle \langle\!\langle F_i F_j \rangle\!\rangle + \langle\!\langle F_i F_j F_k \rangle\!\rangle = \langle\!\langle F_i F_j F_k \rangle\!\rangle.$$

The cumulant expansion of the correlation $\langle F_0 F_0 F_0 F_0 \rangle$, which determines α_4, involves the product of cumulants $\langle\!\langle F_0(t_1)F_0(t_2)\rangle\!\rangle\langle\!\langle F_0(t_3)F_0(t_4)\rangle\!\rangle$ and two similar terms. However, since a product of cumulants depends only on two time differences, the corresponding contributions to the four-dimensional time integral in the expression for α_4 vanish in the limit $\tau \to 0$. Therefore only the cumulant $\langle\!\langle F_0(t_1)F_0(t_2)F_0(t_3)F_0(t_4)\rangle\!\rangle$ contributes the expression for α_4.

The fact that D_4 is linear in cumulants of F_i means that D_4 is a linear functional of cumulants for the density of bath particles $N(z,t) = \sum_i \delta(z - z_i(t))$, where z_i denotes the coordinate-momentum pair (x_i, p_i) of a bath particle. In turn, one can observe that cumulants $\langle\!\langle N(z_1,t_1)N(z_2,t_2)...N(z_k,t_k)\rangle\!\rangle$ of any order k depend linearly on the concentration of bath molecules n. For instance, in the expression for the product $N(z_1,t_1)N(z_2,t_2)$ one can write the double sum as $\sum_{i,j} = \sum_{i\neq j} + \sum_{i=j}$ which gives $\langle N(z_1,t_1)N(z_2,t_2)\rangle = \langle N(z_1,t_1)\rangle\langle N(z_2,t_2)\rangle + \sum_i \langle \delta(z_1 - z_i(t_1))\delta(z_2 - z_i(t_2))\rangle$. Here the second term on the right side is by definition the cumulant $\langle\!\langle N(z_1,t_1)N(z_2,t_2)\rangle\!\rangle$ which is obviously linear in n.

It follows from the above discussion that the operator D_4 depends linearly on the concentration of bath molecules n. In contrast, the first and second terms in $D_2^\star$ are proportional respectively to $\gamma^\star$ and the correlation $\langle F_0(t_1)F^\star(t_2)\rangle$, which are both quadratic in n. The Maxwellian distribution $f_M(p) \sim \exp\left(-\beta p^2/2m\right)$ depends neither on λ nor on n. Therefore, if $f_M(p)$ is a stationary solution of the FPE (27), it must satisfy each term separately:

$$D_2 f_M(p) = 0, \quad D_2^\star f_M(p) = 0, \quad D_4 f_M(p) = 0. \tag{30}$$

The first relation, as was discussed at the beginning of the Letter, is satisfied. The validity of the relation $D_4 f_M = 0$ is not our concern here. One can show that D_4 has the same structure as for the Rayleigh model [3, 4] and the validity of the relation $D_4 f_M = 0$ can be explicitly checked for the extended Rayleigh model [6]. The central result of this Letter is that the second equation $D_2^\star f_M = 0$ is not satisfied. Indeed, this equation implies that $b_1 = \frac{\beta}{m} b_2$, similar to the condition (11) for D_2. Instead, the relation with the additional factor $1/2$ actually holds:

$$b_1 = \frac{\beta}{2m} b_2. \tag{31}$$

Explicitly this relation has the form

$$\int_0^\infty dt C(t) \int_0^\infty dt C(t)t = \frac{1}{2\tau} \int_0^\tau \int_0^\tau dt_1 dt_2 C^\star(t_1, t_2), \tag{32}$$

where $C(t) = \langle F_0(0)F_0(t)\rangle$ and $C^\star(t_1, t_2) = (\beta/m)^{-1}\langle F_0(t_1)F^\star(t_2)\rangle$. According to (19), the latter correlation is given by

$$C^\star(t_1, t_2) = \int_0^{t_2} dt' \, C(t') \int_{t_2-t'}^{t_2} dt'' \, C(|t_1 - t''|). \tag{33}$$

Note that Eq.(32) is an asymptotic relation: the double integral of $C^\star$ must be taken in the limit $\tau \gg \tau_c$. The validity of the relation (32) may be verified directly, for instance, for $C(t) \sim e^{-t/\tau_c}$ or for a Gaussian correlation. A general proof of (32) is rather lengthy and will be presented elsewhere.

Since $D_2^\star f_M(p) \neq 0$, the stationary solution of the FPE (27) is not Maxwellian and in general can not be analyzed without identifying an explicit form of the operator D_4 which is beyond our scope here. Suppose however that the concentration of bath molecules n is in a sense large and $D_4 \sim n$ can be neglected compared to $D_2^\star \sim n^2$. The λ^4-order FPE with D_4

dropped is an equation of second order which has the same structure as the λ^2-order equation (8) but with modified coefficients $a_i^\star = a_i + \lambda^2 b_i$. Its stationary solution $\exp\left(-\frac{a_1^\star}{2a_2^\star}p^2\right)$ is the Maxwellian distribution $\exp\left(-\frac{\beta^\star}{2m}p^2\right)$ but with the inverse temperature $\beta^\star = ma_1^\star/a_2^\star$ slightly lower than that for the bath, β. Taking into account relations (11) and (31), one obtains $\beta^\star = \beta\left(1 - \lambda^2\, b_1/a_1\right)$, or

$$\beta^\star = \beta\left\{1 - \lambda^2\,\frac{\beta}{m}\,\int_0^\infty dt\, C(t)\, t\right\}. \tag{34}$$

This result may be interpreted alternatively as a renormalization of the mass of the B particle $M \to M^\star = (\beta/\beta^\star)M$.

In conclusion, in this Letter we discussed the derivation of the Fokker-Planck equation corresponding to the microscopic Langevin equation of order λ^4. The procedure includes the expansion of the originally non-Markovian Langevin equation around the Markovian limit and evaluation of the coefficients in the Kramers-Moyal expansion of the corresponding master equation. Let us emphasize that the method we used here is not just a truncation of the Kramers-Moyal expansion, which is known to yield an incorrect description. Rather, we transformed the Kramers-Moyal expansion into the expansion in powers of small parameter λ and applied a perturbation technique to obtain an equation to given order in λ. This may be seen as a generalization of van Kampen's $1/\Omega$-expansion [3,4]. It is found that to order λ^4 the method leads to the equation which has a non-Maxwellian stationary solution. This feature originates entirely from non-Markovian corrections collected in the operator $D_2^\star$, Eq.(28). Since the method yields correct results for the Markovian Rayleigh model [4] at least to order λ^4, one may conclude that either the deviation from Maxwellian distribution for conservative Brownian motion is a small but real effect, or the procedure adopted here does not treat non-Markovian effects properly. Note that we assumed but did not prove that each term in λ-expansions is bounded for all t. If the assumption is correct, the results of the Letter would mean that the conventional time-reversal arguments [3], leading to the detailed balance and, eventually, to the H-theorem, do not apply to Brownian motion beyond the lowest order in λ. This is perhaps not such a surprise recalling that the right part of a Langevin equation is not a true force on the particle but rather an approximation to given order in λ. Whether or not this truncated force corresponds to any effective Hamiltonian is not known a priori, and therefore the invariance for time reversal can not be invoked. On the other hand, an *exact* closed equation for a targeted variable is inevitably non-Markovian, and the standard detailed balance arguments can not be applied either. As a referee noted, there is a similarity with the Onsager relations which follow from microscopic reversibility but become only approximately valid when higher order corrections are included in a fast variables elimination scheme [7].

REFERENCES

[1] Cohen E.G.D., *Physica A*, **305** (2002) 19.
[2] Beck C., *Phys. Rev. Lett.*, **87** (2001) 180601; Annunziato M., Grigolini P. and West B., *Phys. Rev. E*, **64** (2001) 011107; Annunziato M., *Phys. Rev. E*, **65** (2002) 021113.
[3] Van Kampen N.G., *Stochastic Processes in Physics and Chemistry*, (North Holland, Amsterdam) 1981.
[4] Plyukhin A.V., *Physica A*, **351** (2005) 198.
[5] Mazur P. and Oppenheim I. , *Physica*, **50** (1970) 241.
[6] Plyukhin A.V. and Schofield J., *Phys. Rev. E*, **68** (2003) 041107.
[7] Hubmer G.F. and Titulaer U.M., *J. Stat. Phys.*, **50** (1988) 913, and references therein.